I. THE VAPOR PHASE CONDENSATION OF BUTADIENE AND PROPIONITRILE

II. PREPARATION OF A COLORED SOLUBLE POLYMER

BY

JESSE CHIA-HSI HWA

B.S., St. John's University, 1945
M.S., University of Illinois, 1947

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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I. THE VAPOR PHASE CONDENSATION OF BUTADIENE AND PROPIONITRILE

Introduction

The principle synthetic rubber currently manufactured in the United States is compounded from the butadiene-styrene copolymer commonly designated as GR-S. This synthetic rubber has certain defects which cause it to be inferior to natural rubber in some properties. During the past few years, various methods to improve the qualities and properties of GR-S have been extensively studied and developed. Among these it has been found that notable improvements in the tensile strength, rebound, aging, cure stability and flex-crack resistance of GR-S were made by substituting 5-15 per cent of styrene by 2-vinylpyridine. (1) The superiority of the copolymer of 2-vinylpyridine and butadiene over GR-S was also observed. (2,3)

Due to the growing importance of and demand for 2-vinylpyridine for the tire industry, a large supply of this compound is needed. At the present moment, the bulk of the commercial 2-vinylpyridine is synthesized by the reaction of α-picoline with formaldehyde followed by dehydration. However the supply of α-picoline from coal tar is limited and, furthermore, the cost of 2-vinylpyridine is too high for practical utilization as a rubber component.

The purpose of this investigation was to devise a new method of making 2-vinylpyridine.

Discussion Of Results

An apparatus designed for the vapor phase reaction of butadiene and propionitrile was arranged according to the scheme of Janz, Ascah and Keenan for the reaction of butadiene with cyanogen. (4) When propionitrile and gaseous butadiene were passed through a hot unpacked tube at 500° to

600° at atmospheric pressure over a contact period of thirty to one hundred and thirty seconds, 2-ethylpyridine and aniline were isolated and identified. The total yield under optimum conditions was about 5 per cent and aniline predominated.

The formation of 2-ethylpyridine was believed to be the result of a Diels-Alder-type condensation of the two reactants followed by dehydrogenation of the adduct. The formation of aniline was explained by the Diels-Alder-type condensation of butadiene with the tautomeric form of propionitrile and the subsequent loss of a methane molecule from the adduct.

When butadiene and acetyl cyanide were allowed to react in the vapor phase at elevated temperatures, no 2-acetylpyridine was formed. No reaction occured when propionitrile and liquid butadiene were allowed to react at 50° in the presence of Friedel-Crafts-type catalysts.

When the vapor phase condensation of propionitrile and butadiene were conducted at 500° in the presence of activated alumina, a mixture of approximately equal amounts of 2-ethylpyridine and an unidentified hydroxypyridine was obtained. No aniline or 2-vinylpyridine was formed. It has been shown that the condensation reaction was dependent not on the mere surface of the catalyst, but rather on the chemical nature and the freshness of the catalyst.

The best yield (7.3 per cent) of the condensation product of butadiene and propionitrile was obtained when an excess of the latter was employed in the presence of aluminum oxide. Condensation reactions in the presence of some other solid catalysts gave lower yields of the product.

By the use of fluid catalyst techniques and a continuous flow system with adequate recovery of reactants, this reaction might be developed into a useful synthetic source of 2-ethylpyridine which can be readily dehydrogenated to 2-vinylpyridine.

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II. PREPARATION OF A COLORED SOLUBLE POLYMER

The present investigation was undertaken at Dr. P. Debye's request for a highly colored soluble polymer having a molecular weight of about 100,000.

The reaction of 2,4-dinitrophenylhydrazine and polymethyl vinyl ketone gave a colored but insoluble polymer. A light colored copolymer was obtained when the copolymerization of methyl vinyl ketone 2,4-dinitrophenylhydrazone and styrene was catalyzed by boron trifluoride. Interaction of styrene-maleic anhydride copolymer and 1-(3-methyl-4-nitrophenyl-azo)-2-naphthylamine at an elevated temperature under vacuum gave a colored but insoluble polymer.

VITA

The author was born in Hankow, China, on July 12, 1924. He attended the Dawson Primary School, Hankow, and Yali Middle School, Changsha, and was graduated from the St. John's Middle School, Shanghai, in August, 1941. In September of that year he enrolled in the St. John's University, Shanghai, and was graduated in January, 1945, with the degree of Bachelor of Science in Chemistry With Honor. In August, 1946 he came to the United States and enrolled in the Graduate School of the University of Illinois the following month. He was granted the degree of Master of Science in Chemistry in June, 1947. He was employed by the General Tire and Rubber Company, Akron, Ohio, from June to August, 1948, as a research chemist. Since February 1947 he has held a Special Research Assistantship in chemistry on the Rubber Research Program of the University.

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